PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

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PCT

NOTIFICATION OF TRANSMITTAL OF THE INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Rule 71.1)

Date of mailing *(day/month/year)*	30.03.2004
Applicant's or agent's file reference: 228	**IMPORTANT NOTIFICATION**

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/EP 02/13329	20.11.2002	10.01.2002

Applicant: UMICORE

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.

2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.

3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. **REMINDER**

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

The applicant's attention is drawn to Article 33(5), which provides that the criteria of novelty, inventive step and industrial applicability described in Article 33(2) to (4) merely serve the purposes of international preliminary examination and that "any Contracting State may apply additional or different criteria for the purposes of deciding whether, in that State, the claimed inventions is patentable or not" (see also Article 27(5)). Such additional criteria may relate, for example, to exemptions from patentability, requirements for enabling disclosure, clarity and support for the claims.

Name and mailing address of the international preliminary examining authority:

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PATENT COOPERATION TREATY

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference 228	**FOR FURTHER ACTION**	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. PCT/EP 02/13329	International filing date *(day/month/year)* 20.11.2002	Priority date *(day/month/year)* 10.01.2002
International Patent Classification (IPC) or both national classification and IPC C23C2/02		
Applicant UMICORE		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 6 sheets, including this cover sheet.

   ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of 4 sheets.

3. This report contains indications relating to the following items:

   - I ☒ Basis of the opinion
   - II ☐ Priority
   - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - IV ☐ Lack of unity of invention
   - V ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
   - VI ☐ Certain documents cited
   - VII ☐ Certain defects in the international application
   - VIII ☐ Certain observations on the international application

Date of submission of the demand	Date of completion of this report
02.07.2003	30.03.2004
Name and mailing address of the international preliminary examining authority: European Patent Office - P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Tx: 31 651 epo nl Fax: +31 70 340 - 3016	Authorized Officer Ovejero, E Telephone No. +31 70 340-2343

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/EP 02/13329

I. Basis of the report

1. With regard to the **elements** of the international application *(Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17))*:

Description, Pages

1, 3-5, 7-12	as originally filed
2, 6	filed with telefax on 18.03.2004

Claims, Numbers

1-13	filed with telefax on 18.03.2004

Claims, Pages

13-14	filed with telefax on 18.03.2004

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

   These elements were available or furnished to this Authority in the following language: , which is:

   ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).

   ☐ the language of publication of the international application (under Rule 48.3(b)).

   ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

   ☐ contained in the international application in written form.

   ☐ filed together with the international application in computer readable form.

   ☐ furnished subsequently to this Authority in written form.

   ☐ furnished subsequently to this Authority in computer readable form.

   ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

   ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

   ☐ the description, pages:

   ☐ the claims, Nos.:

   ☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

   (Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-13
	No:	Claims	
Inventive step (IS)	Yes:	Claims	1-13
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1-13
	No:	Claims	

2. Citations and explanations

   see separate sheet

Re Item V

Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

Reference is made to the following documents:

D1:GB 896 866 A (THE BOLLER DEVELOPMENT CORPORATION).
D2:DATABASE CA [Online] CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; ENDO, EIICHI ET AL: 'Flux for manufacture of Zn-Mg-Al alloy plated steel by dip coating' retrieved from STN Database accession no. 134:196248 CA XP002201101 & JP 2001 049414 A (NIPPON STEEL CORP., JAPAN).

1 NOVELTY (ART. 33(2) PCT)

1.1 Document D.2, which is considered to represent the most relevant state of the art, discloses a process for preparation of a steel sheet surface for hot dip galvanising in a Zn containing molten bath, comprising the steps of degreasing the surface, pickling the surface, and applying a protective layer to the surface by immersion in a flux solution, characterised in that the flux solution comprises a soluble bismuth compound (abstract), from which the subject-matter of claim 1 differs in that a specific cleaning treatment by either one of electrocleaning, ultrasonic cleaning and brush cleaning is performed so as to obtain less than 0.6 $\mu g/cm^2$ residual dirt.

Same argument as above described applies to independent claim 9, where the bath used for hot dip additionally contains Al. Document D.2 discloses a molten Zn-Mg-Al alloy bath for hot dip coating (abstract) but in the previous steps of preparing the steel surface no specific treatment for the cleaning is disclosed as to obtain the level of residual dirt required by the present invention.

The subject-matter of claims 1 and 9 are therefore novel (Article 33(2) PCT).

Dependent claims 2-8 and 10-13 are also new under Article 33(2) given that they refer back to novel independent claims 1 and 9.

2 INVENTIVE STEP (ART. 33(3) PCT)

2.1 The document D.2 is regarded as being the closest prior art to the subject-matter of claim 1, as already explained above w.r.t. novelty (the references in parentheses applying to this document):

The differentiating features of claim 1 concerns the cleaning level to be achieved by the cleaning step, i.e. less than 6 $\mu g/cm^2$ residual dirt.

The problem to be solved by the present invention may therefore be regarded as how to improve the process of cleaning a steel surface prior to hot dip galvanising, such that single dip-Al rich zinc alloy coatings on continuous products can be applied without coating defects.

The solution to this problem proposed in claim 1 of the present application is considered as involving an inventive step (Article 33(3) PCT) for the following reasons:

Although most of the features present in the process of claim 1 are already known by the prior art (D.2, abstract; D.1, page3, l. 70-84, claim 1) there is no teaching in D.2 concerning the importance of extremely clean surfaces for special hot dip galvanising applications. Furthermore, the combination of these known features with the first step of cleaning the surface while reducing the residual dirt to less than 6 $\mu g/cm^2$ followed by pickling before fluxing and hot dipping, does not appear have been suggested in the prior art.

The special cleaning procedure presents specific advantages over the classical processes for hot dip aluminum rich alloys: it guaranties the absence of water breaks on the surface and thereby avoids the occurrence of bare spots, pinholes and other defects in the final coated surface. The disclosure of the minimum level of cleanness to obtain successful results for this material after hot dip is not obvious from the teaching of the prior art.

In the same way, the application of the cleaning step disclosed in independent claim 1 to a single-dip galvanising process using an aluminium containing bath disclosed in

independent claim 9 of the present application, presents the same advantages to those above described for a general hot dip process.

To an excellent quality of the final galvanised surface it is added the economical aspect of allowing a successful employment of the single-dip process instead a double-dip process.

Claims 2-8 and 10-13 are dependent on claim 1 and 9 respectively and as such also meet the requirements of the PCT with respect to novelty and inventive step.

3 INDUSTRIAL APPLICATION (ART. 33(4) PCT)

The invention is considered to be industrially applicable in the field of hot-dip galvanising of metals and steels: it allows the simplification of the conventional process (from double dip process to a single dip process) and gives rise to a good final quality of the coating.

and pickling, absence of flux drying and preheating, when cold and sometimes wet parts are immersed in molten zinc.

Aluminium creates three main technological problems, which complicate the galvanising process:

- moisture or iron oxides on the steel surface reacts with molten aluminium and creates aluminium oxides, which are not wetted by molten zinc, according to the following reactions:

$$3\ H_2O + 2\ Al \quad ? \quad 3\ H_2? + Al_2O_3$$

$$3\ FeO + 2\ Al \quad ? \quad 3\ Fe + Al_2O_3$$

$$3\ Fe_3O_4 + 8\ Al \quad ? \quad 9\ Fe + 4\ Al_2O_3 \quad ;$$

- a thin layer of zinc-aluminium oxides on the surface of molten bath unavoidably contacts the steel in the dipping area and degrades its wetting by molten zinc;

- the aluminium present in the molten zinc reacts with the flux and consequently deteriorates its effectiveness according to the reactions:

$$3\ ZnCl_2 + 2\ Al \quad ? \quad 3\ Zn + 2\ AlCl_3?$$

$$6\ NH_4Cl + 2\ Al \quad ? \quad 2\ AlCl_3? + 6\ NH_3 + 3H_2?.$$

These peculiar features of galvanising in the presence of aluminium create unsatisfactory coatings with bare spots, pinholes and surface roughness.

It is thus an aim of this invention to alleviate the problems as described above.

To this end, a process is disclosed for the preparation of a steel surface for single-dip aluminium-rich zinc galvanising comprising the steps of cleaning the surface so as to obtain less than 0.6 $\mu g/cm^2$ residual dirt, pickling the surface, and applying a protective layer to the surface by immersion in a flux solution comprising bismuth. The cleaning is performed by either one of electrocleaning, ultrasonic cleaning and brush cleaning. When using electrocleaning, at least 25 C/dm^2 can be passed through the steel surface. The pickling can be performed by either one of electropickling,

trivalent ferric cation Fe^{3+} can be reduced to metal iron at +0.33 V. So, if in acid solution, which contains Fe^{3+}, a steel sample is immersed, two reactions take place:

- metal iron is dissolved and creates ferrous cation Fe^{2+}

$$Fe^0 - 2e \rightarrow Fe^{2+} \quad ; \text{ and}$$

- ferric iron Fe^{3+} is reduced to metal iron

$$Fe^{3+} + 3e \rightarrow Fe^0 \quad .$$

For every 3 created ferrous ions 2 ferric ions become metallic. The reaction is very rapid, because its electromotive force is high:

$$E = E(Fe/Fe^{3+}) - E(Fe/Fe^{2+}) = 0.33\ V - (-0.44\ V) = 0.77\ V$$

As a result, the concentration of ferric ion in the pickling solution gradually drops, while the amount of ferrous ion proportionally increases. To keep the solution in equilibrium, the ferrous ions have to be oxidised, which can be done with any oxidiser or which can happen naturally by air oxygen.

The described phenomenon was used in an accelerated pickling procedure: wire from low and high carbon steel was pickled in 18.5 % HCl solution for 3 to 5 sec., rinsed and immersed for 3 to 5 sec. in 10 % $FeCl_3$ solution at 50 °C. The sample surface became uniformly grey. The wire samples were then rinsed, fluxed, dried and preheated, and were then easily coated by Galfan without any defects.

A good fluxing agent for Galfan should be able:

- to create a thin protective metallic layer on the steel surface without applying electricity (no electroplating);
- to protect this layer and steel substrate from oxidation during drying/heating;
- to be easily removable from steel surface in molten Galfan.

In regular galvanising, ammonium chloride is present in the flux, and fulfils two functions, one of them being the reduction of iron oxides and the other one the flux removal from the steel surface by generating an energetic gaseous torrent through the molten zinc. In a Galfan coating process the first function is almost nullified because of the strong aluminium affinity to chlorine. The opinion was established that specifically the $AlCl_3$ formed deteriorates the Galfan coating, thereby creating pinholes and uncoated spots. So, the idea

Claims

1. Process for the preparation of a steel surface for hot-dip galvanising in a zinc based molten bath, comprising the steps of cleaning the surface, pickling the surface, and applying a protective layer to the surface by immersion in a flux solution, characterised in that

the cleaning is performed so as to obtain less than 0.6 $\mu g/cm^2$ residual dirt, and

the flux solution comprises a soluble bismuth compound

2. Process according to claim 1, characterised in that the cleaning is performed by either one of electrocleaning, ultrasonic cleaning and brush cleaning

3. Process according to claim 1, characterised in that the cleaning is performed by electrocleaning, whereby at least 25 C/dm^2 is passed through the steel surface

4. Process according to claim 1, characterised in that the pickling is performed by either one of electropickling, ultrasonic pickling and ion exchange pickling using an Fe(III) chloride solution

5. Process according to claims 1 to 4, characterised in that the soluble bismuth compound is an oxide, a chloride or a hydroxychloride

6. Process according to claims 1 to 5 characterised in that the flux is an aqueous solution comprising between 0.3 and 2 wt% of bismuth

7. Process according to claims 1 to 6 characterised in that the flux solution further comprises at least 7 wt% of NH_4Cl

8. Process according to claim 7 characterised in that the flux solution comprises between 8 and 12 wt% of NH_4Cl

9. Process according to claims 7 or 8, characterised in that the flux solution further comprises between 15 and 35 wt% of $ZnCl_2$

10. Process for single-dip galvanising of steel using an aluminium containing molten zinc baths, whereby the steel surface is prepared according to claims 1 to 9

11. Process according to claim 10, whereby the aluminium containing zinc bath further contains at least 0.15 % Al, and preferentially between 2 and 8 wt% Al

12. Process according to claim 11 whereby the aluminium containing zinc bath is a Galfan bath

13. Process according to claims 1 to 12, characterised in that the steel is in the form of a continuous product

14. Process according to claim 13, characterised in that the continuous product is steel wire, tube or plate

15. A continuous steel product coated with a metallic layer consisting of bismuth